

**THERMAL DECOMPOSITION CHEMISTRY OF  
POLY(VINYL ALCOHOL): CHAR CHARACTERIZATION**  
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Currently, due to concerns over the environmental effects of halogenated compounds, there is an international demand for the control of polymer flammability without the use of halogenated or metal based additives.<sup>1,2</sup> Our approach to this issue is first to characterize the fundamental condensed phase processes and structures which lead to char formation during polymer combustion and then, to use this information to design new strategies, that do not use halogenated additives, which increase char formation and therefore will reduce polymer flammability.<sup>3,4</sup>

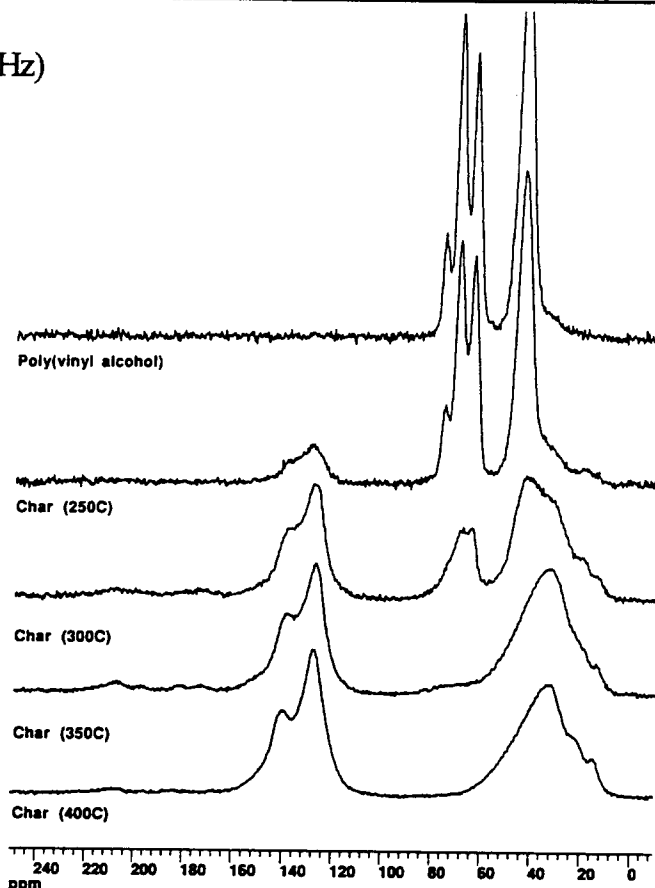
The polymer we chose to investigate was poly(vinyl alcohol), PVA, because of its linear aliphatic structure, low char yield and commercial applications (paper, textile and adhesives). The thermal decomposition of PVA has been studied both in the gas and condensed phases, however, only limited characterization of PVA chars exists.<sup>5,6,7</sup> We prepared PVA chars in a flow pyrolysis apparatus with an inert atmosphere (N<sub>2</sub>) at several temperatures. This experimental setup allows study of the condensed phase decomposition processes in the absence of gas phase oxidation.<sup>8</sup> Upon heating PVA above the decomposition temperature the polymer begins a rapid chain-stripping elimination of H<sub>2</sub>O.<sup>9,10</sup> This process coupled with melting causes the material to foam or intumesce as it decomposes. As a result most of the chars are rigid foams. The physical appearance, hydrogen-to-carbon ratio and char yields are shown in Table 1.

Table 1. Material	Appearance	H/C Ratio	Char Yield (%)
PVA	white solid	2:1	NA
250 °C Char (30 min)	yellow-orange foam	1.9:1	60
300 °C Char (30 min)	tan rigid foam	1.4:1	47
350 °C Char (30 min)	dark brown foam	1.2:1	17
400 °C Char (30 min)	black powder	1:1	5

The chars were characterized using CP/MAS <sup>13</sup>C NMR. Figure 1 shows the PVA and char NMR spectra. The preliminary results suggest that during the well known chain-stripping elimination reaction of PVA a random chain scission reaction is also in progress. We also see evidence of formation of carbon-carbon bonds (non-protonated (substituted) olefinic/aromatic carbons) at all char temperatures. At temperatures up to 350 °C the polyene products from the elimination reaction are converted into aliphatic groups, possibly via Diels-Alder and/or radical reactions. Even in chars formed at 400 °C almost all of the aliphatic carbons are protonated. It appears that these chars retain a significant amount of hydrogen since the H:C ratio is as high as 1:1 at 400°C.

We plan to utilize FTIR, and other spectroscopic techniques to further characterize the decomposition of PVA and of PVA with char enhancing additives.

Figure 1.  
 $^{13}\text{C}$  NMR (25 MHz)  
 1ms CP time  
 3 sec rep time  
 4 kHz MAS



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